

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Process for Producing β -Methylmercaptopropionaldehyde

We, SHIOTOMO CHEMICAL COMPANY LTD., a Japanese Body Corporate of 15, Kitahama-Schome, 11-gashi-ku, Osaka, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, is to be particularly described in and by the following statement:

This invention relates to a process for producing β -methylmercaptopropionaldehyde (hereinafter referred to as "M-aldehyde") by reacting acrolein with methylmercaptan in the presence of a catalyst. M-aldehyde is an important intermediate in the synthesis of methionine, which is an essential amino acid, for example by treating it with (a) ammonium carbonate or bicarbonate, or ammonia and carbon dioxide, and (b) hydrocyanic acid or cyanide and hydrolysing the resulting 5-(β -methylmercaptoethyl) hydrantion (see for example, United States Specification No. 2,557,913).

Heretofore, M-aldehyde has been obtained by reacting methylmercaptan with high purity acrolein containing at least 95% by weight of acrolein in the presence of a catalyst at a temperature of -5° to 120°C . in a yield of at least 95%, based on the acrolein. In this process, however, the high purity acrolein reacts rapidly to generate a considerable heat of reaction, and impurities are liable to be formed due to this reaction heat. In addition, in the purification concentration step for preparing the high purity acrolein from crude aqueous acrolein solutions, the loss of acrolein due to polymerisation or dissolution is considerable and the yield of acrolein in this step is ordinarily not more than 50 to 80%.

Commercially, acrolein is prepared either by condensing formaldehyde with acetal-

dehyde or by oxidizing propylene with oxygen or air. In either process, the resulting gas is condensed or absorbed in water to obtain a dilute aqueous acrolein solution (hereinafter referred to as "crude aqueous acrolein solution") which contains, in addition to about 1-30% by weight of acrolein, large quantities of aldehydes such as formaldehyde, acetaldehyde and propionaldehyde, unsaturated organic acids, ketones, water, and other impurities such as high boiling materials.

The purification concentration treatment of the crude aqueous acrolein solution is carried out by first distilling out acrolein, containing acetaldehyde and small amounts of propionaldehyde, acetone and water and then removing acetaldehyde from the distillate by distillation, followed by removal of polymers and a small amount of water. In this treatment, the concentrated acrolein is necessarily heated in the still portion, particularly in the rectification or distillation step for removing acetaldehyde. Therefore, the acrolein tends to deteriorate in this portion from denaturation due to dimerization or polymerisation, and it is thus necessary to use a large amount of a stabilizer for the acrolein. Further, in order to remove the polymers formed in the rectification step, the acrolein has to be subjected to further purification. We have found that in the purification concentration treatment of such a crude aqueous acrolein solution to produce a high purity acrolein at a concentration of, for example, about 95% by weight; about 10-50% by weight of acrolein is lost, particularly in the rectification step for removing acetaldehyde, and in the rectification or distillation step for removing polymers and the like. In these purification steps, not only is the amount of acrolein lost considerable

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but also the distillation columns tend to become clogged due to the presence of polymers and the like, and therefore continuous operations over a long period of time become difficult.

In order to avoid the acrolein loss in the purification concentration step, a process has been proposed (in Japanese Patent Publication No. 19090/65) for producing 10 M-aldehyde, in which a crude aqueous acrolein solution containing 1-40% of acrolein is used, without rectification, as a starting material and this is reacted with methylmercaptan at a temperature of -5 15 to 50°C. in the presence of an organic base, as catalyst, having a dissociation constant at 25°C. not greater than 2×10^6 . In this process, however, methylmercaptan is used in an amount (in moles) about 3 20 times the amount of acrolein. As is clear, the wastage of methylmercaptan is considerable and the catalyst system, which may be used, is necessarily restricted. The yield of M-aldehyde is low in the case 25 where methylmercaptan is used in less than an equimolar amount of acrolein. Further, since complex impurities are formed, difficulties accompany the preparation of high purity M-aldehyde, and many difficulties 30 accompany the production of high purity methionine from the M-aldehyde produced.

It is an object of the present invention to provide a process for producing M-aldehyde in high yield by reacting methylmercaptan with an acrolein-containing solution prepared simply by purifying a crude aqueous acrolein solution, without loss of acrolein, which process reduces or overcomes the drawbacks of conventional processes.

According to the present invention, there is provided a process for producing high purity M-aldehyde which comprises reacting, in the presence of a catalyst such as 45 an organic base, a combination of an organic base and an acid, an organic peroxide, mercury methylmercaptide or cupric acetate, methylmercaptan and acrolein, the acrolein being present as a solution which 50 comprises acrolein, water and at least one carbonyl compound which is an aliphatic saturated aldehyde or aliphatic saturated ketone, which solution is free from unsaturated organic acids.

55 In accordance with the process of the present invention, the amount of acrolein lost in the purification step for removing from the crude aqueous acrolein solution the main components which have a 60 higher boiling point than acrolein is relatively small. Therefore, when there is used, as starting material, an acrolein-containing solution comprising acrolein, water and at least one carbonyl compound which is an 65 aliphatic saturated aldehyde or aliphatic

saturated ketone, from which solution have been removed the main components having a higher boiling point than acrolein, not only is the loss of acrolein which arises in the production of high purity acrolein 70 reduced but also the effect of the heat of reaction is reduced owing to the presence of the solvents, so that the denaturation and polymerisation of acrolein is reduced 75 or eliminated.

Moreover, as M-aldehyde has a higher boiling point, and is more stable, than acrolein, the compounds other than acrolein which are present in the acrolein-containing solution are more easily separated from the resulting crude M-aldehyde 80 than in the case where it is separated directly from the acrolein-containing solution, with a result that the rectification of the crude aqueous acrolein solution is simplified with a consequent decrease in the loss of acrolein.

The acrolein-containing solution employed as starting material in the process of the present invention may be a solution 90 obtained by condensing or water-treating an acrolein-producing reaction gas and purifying the resulting crude aqueous acrolein solution so that the solution comprises (a) acrolein, (b) water, and 95 (c) at least one carbonyl compound which is an aliphatic saturated aldehyde or an aliphatic saturated ketone.

The acrolein-containing solution employed in the present process ordinarily 100 contains 50-90% by weight of acrolein. If a solution having an excessively high acrolein concentration is used, it is difficult to purify the crude aqueous acrolein solution so that some acrolein is lost. 105 When the concentration is low, injuries impurities tend still to be present and the rate of reaction for the formation of M-aldehyde is reduced.

The use of an acrolein-containing solution containing these components is advantageous for several reasons. For example, not only can the purification treatment adopted in preparing such a solution from a crude aqueous acrolein solution 110 be simplified as compared with the purification treatment involved in the production of high purity acrolein, but also the loss of acrolein due to polymerisation in this 115 purification treatment can be reduced considerably, without involving subjecting acrolein to rigorous purification conditions. Generally, the loss of acrolein due to polymerisation is not more than about 5%. Another advantage is that acrolein is added 120 in a dilute form so that rapid reaction of acrolein can be prevented and a rapid increase of temperature avoided. The reaction to produce M-aldehyde is highly exothermic and, further, acrolein is a very un- 130

stable compound and is readily denatured or polymerised. Therefore, the reaction temperature should be controlled. This is possible with the process of the present invention, with the result that the yield of M-aldehyde, based on the acrolein, can be 95 to 99%.

Suitable carbonyl compounds which may be used in the process include formaldehyde, acetaldehyde, propionaldehyde and acetone. These carbonyl compounds do not effect the reaction to produce M-aldehyde and can be more readily separated from the resulting M-aldehyde solution than 15 during the purification of an acrolein-containing solution. Therefore, the amount used is not particularly critical. However, since an acrolein-containing solution obtained by purifying a crude aqueous 20 acrolein solution ordinarily contains from about 1 to 15% by weight of such a carbonyl compound, it is convenient to use, as such, an acrolein-containing solution having a carbonyl compound content within 25 in this range. However, to increase the solvent effect, the carbonyl compound may be added separately to an acrolein-containing solution to increase the proportion of carbonyl compound. If the carbonyl compound content becomes excessively high, however, a large volume reactor is required and other operational disadvantages are introduced and, therefore, it is desirable to control the carbonyl compound content, suitably so that it does not exceed 45%.

Further, small amounts of water do not inhibit the formation of M-aldehyde. However, when a large proportion of water is 40 present in the starting acrolein-containing solution, an excessive amount of methylmercaptan is necessary in order to avoid hydration of the acrolein. In such a case, therefore, not only is the wastage of methylmercaptan increased but also the excess of methylmercaptan migrates into the resulting M-aldehyde, either as such or in a combined state with the M-aldehyde, and this is liable to cause difficulties in the 45 purification of the M-aldehyde. Further, the production of high purity methionine also becomes difficult. It is therefore desirable that the water content be kept low and it is preferable to use an acrolein-containing solution having a water content such that, in general, two layers do not form an acrolein-containing solution layer and a water layer containing a small amount of acrolein. Preferably, the water 50 content is less than about 15% by weight. Ordinarily, an acrolein-containing solution obtained by the purification of a crude aqueous acrolein solution has a water content of 1-15% by weight, and it is preferred 55 to use an acrolein-containing solution hav-

ing a water content within this range.

The acrolein-containing solution used in the process of the present invention comprises acrolein, carbonyl compound and water; an unsaturated organic acid should 70 not be present. This is because such acids form complex impurities in the reaction system, thus making it difficult to obtain high purity M-aldehyde. The presence of 75 a saturated organic acid in the acrolein-containing solution is not objectionable, but such an acid is generally removed together with the unsaturated organic acid.

The acrolein-containing solution employed in the process is ordinarily obtained 80 by catalytically oxidizing propylene or by condensing formaldehyde with acetaldehyde and dehydrating the condensate to form an acrolein-containing reaction gas, and condensing the gas, or subjecting the 85 gas to water absorption, to form a crude aqueous acrolein solution, followed by distillation.

Propylene may be oxidized for this purpose over a catalyst with air or oxygen in 90 the presence of a diluent such as steam or nitrogen, ordinarily at a temperature of 230° to 500°C. and 0.1-10 atm. pressure. Preferred catalysts include a bismuth 95 phosphomolybdate system, a copper system or a tellurium system. For the formation of acrolein from formaldehyde and acetaldehyde, there is usually employed a process in which an approximately 30% aqueous formaldehyde solution and acetaldehyde are passed as a gas at about 100 280°-320°C. over silica gel impregnated with an alkali. The former process is more frequently adopted.

The crude aqueous acrolein solutions 105 obtained by these processes ordinarily contain, in addition to 1-30% by weight of acrolein, aldehydes such as formaldehyde, acetaldehyde and propionaldehyde, unsaturated organic acids such as acrylic 110 acid, ketones such as acetone, water and high boiling materials.

The acrolein-containing solution employed in the present process is easily obtainable by subjecting the crude aqueous 115 acrolein solution to a rectification treatment either at atmospheric pressure or under reduced pressure, the top of the distillation column being at a temperature of 55°C. or below. The distillate obtained 120 in this case nearly always has a water content up to 15% by weight and contains no unsaturated organic acid. Thus, a large amount of water and high boiling materials are left in the residue, and these 125 can readily be removed. The rectification may be carried out effectively by using a packed column, a plate tower or other column conventionally employed for ordinary rectification procedures. In such a 130

rectification treatment, the amount of acrolein lost can be adjusted to 5% or less.

The production of M-aldehyde from the acrolein-containing solution is readily achieved under conventional reaction conditions, i.e. at a temperature of -5° to $120^{\circ}\text{C}.$, at atmospheric pressure or below. Suitable catalysts which may be used include organic bases such as pyridine, quinoline and triethylamine; combinations of an organic base and an acid, which are preferred, such as formic, acetic and benzoic acid; organic peroxides such as benzoyl peroxide; mercury methylmercaptide; and cupric acetate.

In view of its specificity the reaction can be carried out in accordance with any known procedure. Thus, methylmercaptan may be incorporated in the acrolein-containing solution, the acrolein-containing solution incorporated in a methylmercaptan liquid or some of the M-aldehyde product may be recycled to the reaction zone and the acrolein-containing solution, methylmercaptan and catalyst component introduced little by little. Alternatively, the process described in our Application No. 140,64/67 (1,150,252) may be used. This process comprises (1) reacting methylmercaptan with β -methylmercaptopropionaldehyde at a temperature of 10 to $90^{\circ}\text{C}.$ and using at least one mole of β -methylmercaptopropionaldehyde per mole of methylmercaptan, and (2), after the generation of heat of reaction in step (1) is substantially complete, reacting the reaction mixture from step (1) with acrolein, in the presence of a catalyst at a temperature of 10 to $100^{\circ}\text{C}.$ for a time of 1 to 180 minutes. The reaction can be carried out not only in a batchwise manner but also in a continuous manner. Any of these procedures may be adopted as occasion demands.

The ratio of acrolein to methylmercaptan in the reaction mixture is suitably from 0.8:1 to 1.2:1. However, the use of excess of acrolein is preferred in that it then becomes possible to produce essentially methylmercaptan-free high purity M-aldehyde and, subsequently, high purity methionine.

Crude M-aldehyde formed in this reaction may be rectified under reduced pressure according to ordinary procedures to obtain high purity M-aldehyde. Since the crude M-aldehyde does not contain impurities which cause particular difficulties during rectification, the rectified M-aldehyde has both improved purity and yield. The following Examples further illustrate the present invention.

EXAMPLE 1

Propylene was oxidized with air in the presence of water vapour and the gaseous

mixture was dissolved into water ($20^{\circ}\text{C}.$), containing hydroquinone, to yield a crude aqueous acrolein solution having the composition shown in the Table 1.

TABLE 1

Component	Weight %
Acrolein	2.21
Acetaldehyde	0.29
Propionaldehyde	0.02
Acetone	0.01
Hydroquinone	0.002
Water	97.48

The crude aqueous acrolein solution was preheated at $89^{\circ}\text{C}.$ and supplied to a rectification column at a rate of 18 kg./hr. It was rectified under atmospheric pressure with the temperature of the column top being $52^{\circ}\text{C}.$, and reflux liquid (the amount of liquid refluxing back) was 1.8 kg./hr.

In this rectification the effluent vapour was cooled and condensed in the presence of hydroquinone, giving an acrolein-containing solution having the composition shown in the Table 2 at the rate of 459 g./hr. The rectification yield of acrolein was 90.96%.

TABLE 2

Component	Weight %
Acrolein	83.10
Acetaldehyde	12.20
Propionaldehyde	0.60
Acetone	0.50
Hydroquinone	0.10
Water	3.50

Into a 500 ml. four necked flask equipped with a stirrer, a thermometer and a feed-pipe 169 g. of the acrolein-containing solution having the composition shown in the Table 2 was charged, and the flask was dipped in a bath kept at a constant temperature of $5^{\circ}\text{C}.$

After the solution had been cooled sufficiently, 1.8 g. of a catalyst consisting of 40 wt. % of pyridine and 60 wt. % of acetic acid was charged thereto. Then, 123 g. of gaseous methylmercaptan having a purity of 98 wt. % was blown into the mixture, while keeping the mixture at $5 \pm 5^{\circ}\text{C}.$ After the blowing had been completed the reaction mixture was stirred for 3 hours, allowing the mixture to stand at room temperature ($20 \pm 3^{\circ}\text{C}.$). Thus, 293 g. of a product which consisted of 85.70 wt. % of M-aldehyde, 7.02 wt. % of acetaldehyde, 0.35 wt. % of propionaldehyde, 0.29 wt. % of acetone, 2.01 wt. % of water and the remainder high boiling point substances, was obtained. The yield of M-aldehyde was 96.3% based on the acrolein.

It was observed that components other than acrolein in the acrolein-containing

solution had not been changed at all during the reaction.

The reaction product was rectified under a reduced pressure of 30 mm.Hg, the temperature of the top of the rectification column being 10°C., whereby components having a lower boiling point than M-aldehyde were removed, and then rectified at a reduced pressure of 10 mm.Hg and a fraction boiling at 61°C./10 mm.Hg was collected; 243 g. of M-aldehyde having 99.3 wt. % purity was thus obtained.

Comparative Experiment

The acrolein-containing solution obtained in Example 1 was rectified further. That is, the acrolein-containing solution as shown in Table 2 was preheated at 38°C. and was fed into a rectification column at the rate of 400 g./hr. and rectified under atmospheric pressure in the presence of hydroquinone with a column top temperature of 21°C. with reflux liquid of 440 g./hr., whereby the components having boiling points lower than that of acrolein were removed.

Then the acrolein was separated from the components having boiling points higher than that of acrolein by distillation under a reduced pressure of 100 mm.Hg, the column top temperature being 5°C. and with a reflux liquid of 310 g./hr.

The effluent acrolein vapour was cooled and condensed in the presence of hydroquinone, whereby a high purity acrolein having the composition shown in the Table 3 was obtained at a rate of 281 g./hr. The rectification yield was 82%. Accordingly, the overall distillation yield in obtaining the high purity acrolein from the crude aqueous acrolein solution was 78%.

TABLE 3

Component	Weight %
Acrolein	97.00
Acetaldehyde	0.92
Propionaldehyde	0.78
Acetone	0.22
Hydroquinone	0.10
Water	0.98

M-aldehyde was synthesized in a similar way to that described in Example 1 except that 144.8 g. of the purified acrolein shown in Table 3 was used. In this case 269 g. of reaction product was obtained, in which 92.2 wt. % was M-aldehyde and the remainder was higher and lower boiling materials. The yield of M-aldehyde based on acrolein was 95.1%.

The reaction product was rectified under a reduced pressure of 30 mm.Hg and a rectification column top temperature of 10°C., whereby the components having boiling points lower than M-aldehyde were removed, and then rectified under a reduced

pressure of 10 mm.Hg and a fraction having a boiling point of 61°C. 10 mm.Hg was collected; 227 g. of M-aldehyde having a purity of 99.0% was obtained.

EXAMPLE 2

A 500 cc. four-necked flask provided with a stirrer, a thermometer, an inlet tube and a dropping funnel was charged with 200 g. of 99.5 wt. % purity M-aldehyde, and the whole apparatus was immersed in a thermostat at 10°C. After the flask had been cooled thoroughly, 49 g. of 98 wt. % purity methylmercaptan gas was injected while stirring the contents and maintaining the temperature of the contents at 10° ± 5°C. Subsequently, 0.3 g. of acetic acid and of pyridine were charged. Thereafter, 98 g. of an acrolein-containing solution comprising 60 wt. % acrolein, 30 wt. % acetaldehyde, 5 wt. % water and 5 wt. % acetone was added dropwise while stirring the contents. During the addition, the temperature of the contents was maintained at 10° ± 5°C. After completion of the dropwise addition, the stirring was continued for a further 3 hours to obtain 347.5 g. of product. This product was analyzed by gas chromatography; it contained 87.0 wt. % M-aldehyde, 8.47 wt. % acetaldehyde, 1.40 wt. % acetone, 1.43 wt. % water and 0.85 wt. % acrolein. The yield of M-aldehyde, based on the methylmercaptan, was 99%. During the reaction, the components other than acrolein, which had been contained in the initial acrolein-containing solution, were unaffected. The product was rectified under a reduced pressure of 10 mm.Hg and fractions boiling at 61°C. were collected to obtain 300 g. of 99.5 wt. % purity M-aldehyde.

EXAMPLE 3

A reaction tank, a pump, a cooler and a packed column were connected up in a cyclic arrangement to provide a synthesis reactor. In the recycle system, the top of the packed column was open to air. Into the reactor, 1.5 l. of M-aldehyde (purity 99.5 wt. %) was charged and recycled at a rate of 45 l./h. The temperature in the system was maintained at 45° ± 5°C. with the aid of a cooler. Into the reaction tank, 725 g./h. of 99.5 wt. % purity methylmercaptan was injected as a gas. At the same time, 1,063 g./h. of an acrolein-containing solution (82.10 wt. % acrolein, 14.21 wt. % acetaldehyde, 0.65 wt. % acrolein, 14.21 wt. % acetaldehyde, 0.65 wt. % propionaldehyde, 0.21 wt. % acetone and 2.83 wt. % water) was fed to the pipe between the cooler and the packed column. Further, 9 g./h. of a catalyst comprising 50 wt. % acetic acid and 50 wt. % pyridine was fed to the pipe immediately after the acrolein-containing solution inlet, and reaction ensured. The resulting crude M-aldehyde was

withdrawn through an outlet in the pipe positioned after the catalyst inlet. The average amount withdrawn after 10 hours' continuous operation was 1,781 g./h. The amount of M-aldehyde in the product liquid withdrawn was 86.42 wt. % and the yield, based on the methylmercaptan, was 98.6%. The product was rectified under a reduced pressure of 10 mm.Hg and fractions at 61°C. were collected to obtain 99.4% purity M-aldehyde.

WHAT WE CLAIM IS:—

1. Process for the production of β -methylmercaptopropionaldehyde which 15 comprises reacting, in the presence of a catalyst, methylmercaptan and acrolein, the acrolein being present as a solution which comprises acrolein, water and at least one carbonyl compound which is an 20 aliphatic saturated aldehyde or aliphatic saturated ketone, which solution is free from unsaturated organic acids.
2. Process according to claim 1 wherein the said solution consists essentially of acrolein, water and one or more 25 said carbonyl compounds.
3. Process according to claim 1 or 2, wherein the said solution contains 50-90% by weight of acrolein.
- 30 4. Process according to claim 1, 2 or 3 wherein the said solution contains 1-15% by weight of water.
5. Process according to any one of the preceding claims wherein the said solution 35 contains 1-45% by weight of the carbonyl compound.

6. Process according to any one of the preceding claims wherein the said solution is a distillate obtained by rectifying, in a distillation column having a top temperature of 55°C. or below, a crude aqueous acrolein solution formed by absorbing in water a gas resulting from the catalytic oxidation of propylene.

7. Process according to any one of the preceding claims wherein the said solution contains one or more of formaldehyde, acetaldehyde, propionaldehyde and acetone.

8. Process according to any one of the preceding claims wherein the catalyst comprises an organic base and an acid.

9. Process according to any one of the preceding claims wherein the molar ratio of acrolein to methylmercaptan is 0.8:1 to 1.2:1.

10. Process according to claim 1 substantially as hereinbefore described.

11. Process according to claim 1 substantially as described in any one of the foregoing Examples.

12. β -Methylmercaptopropionaldehyde produced by a process as claimed in any one of the preceding claims.

13. Methionine produced in a manner known *per se* from β -methylmercaptopropionaldehyde as claimed in Claim 12.

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